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EVOLUTION OF AMMONIA FROM TYPE ASC WHETLERITE

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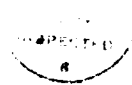
PREFACE

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EVOLUTION OF AMMONIA FROM TYPE ASC WHETLERITE

1. INTRODUCTION

The military uses activated charcoal in gas mask and collective protection filters for removing toxic agents from air. The removal/detoxification process is thought to proceed through physical adsorption followed by chemical reaction such as oxidation¹ and/or hydrolysis. Metal ions are added to the charcoal as impregnants to promote chemical transformation of the adsorbed low molecular weight toxicants. Among these metallic impregnants, copper and chromium are important for removing agents such as CK [Cyanogen Chloride (CNCl)] and AC [Hydrogen Cyanide (HCN)]. The impregnation process which has been optimized through trial and error,² involves the use of ammoniacal solutions of these metal ions and subsequent air drying at elevated temperatures. Most of the ammonia used is often lost during the drying process. However, a definite amount of ammonia is retained on the impregnated charcoal and under certain conditions often undergoes desorption. Recently, the release of ammonia from the impregnated charcoal has been an increased concern. The person donning the gas mask suffers respiratory irritation that has created doubts about the integrity of the mask.

This report reviews the existing literature on the role of ammonia in ASC whetlerite and discusses ammonia's need and role in the detoxification process. A description of the preliminary study that shows that the ammonia is, probably, generated during the oxidative detoxification of AC, and CK follows the review. The report concludes with recommendations for future research to obviate the ammonia problem.

2. SUMMARY LITERATURE REVIEW

2.1 Need for Ammonia in Whetlerite.

During the initial stages of whetlerite* development, the activated charcoal was impregnated using solutions of copper sulfate.² Hot caustic soda was used for making whetlerite Type A along with the copper sulfate solutions, and finely divided metal ions such as iron or zinc were used for making whetlerite Type B. After impregnation, the charcoal was allowed to dry at 350 °C. This impregnation process was believed to result in reducing the copper compound (CuSO₄) to cuprous oxide and metallic copper. Although the copper oxide was useful, metallic copper deposits were not considered necessary for agent detoxification. Later investigations showed that copper oxide alone could be deposited on charcoal using copper amine carbonate instead of copper sulfate and heating copper oxide to a much lower temperature (150 °C). This type of impregnation was very effective; therefore, the charcoal impregnating process using copper carbonate (a sparingly water soluble compound) and a mixture of ammonia and ammonium carbonate was developed and became part of the U.S. Army directive for Type ASC whetlerite production. The ammonia present in the impregnating solution is needed to solubilize the copper ions. The carbonate ions seem to be needed to solubilize the chromate ion.³

*Whetlerite is the name used for activated impregnated charcoal. Both type A and type B whetlerite contained copper in the early days.

2.2 Nature of Ammonia in Freshly Prepared Whetlerite.

During the early stages of Type ASC whetlerite's development, ammonia in the form of ammonium hydroxide and ammonium carbonate was used to solubilize metal ions and keep them in solution during impregnation. The whetlerite activation by drying at elevated temperatures did not remove all the ammonia [conversation with R. Morrison, U.S. Army Chemical Research, Development and Engineering Center (CRDEC)]. Subsequent careful analysis of the whetlerite samples has led to the identification of several metal-ammonium complexes,⁴ which are proposed to play a significant role in the deactivation of toxic agents such as CK. Thus, a simple role of solubilization and ammonia is required to form catalytically active sites on activated charcoal.

2.3 Role of Ammonium Carbonate in Whetlerite.

As stated earlier, ammonium carbonate is used as one of the ingredients for impregnating charcoal with metal ions. Ammonium carbonate was used through a trial and error approach in the early days of whetlerite development, but subsequent research has shown that ammonium carbonate is indeed essential to prepare whetlerite with outstanding CK lives.^{2,4} The role of ammonium carbonate seems to be intimately associated with the efficacy of the detoxification by the metal ions. Pytlewski⁴ and Hammarstrom⁵ postulate that ammonium carbonate plays the following four major roles in whetlerite:

- Base buffer
- Complexation with copper for pore deposition
- Formation of a catalytically reactive compound such as brochantite chromate
- Complexation of Cr^{+6} with carbonate ion to form $(\text{CrO}_3\text{-CO}_3)^{-2}$

The whetlerizing solution possibly contains several ions such as $\text{Cu}(\text{NH}_3)_4^{+2}$, NH_4^+ , $\text{Cr}(\text{NH}_3)_6^{+3}$, CrO_4^{-2} , CO_3^{-2} , OH^- , and aqueous ammonia. The ammonium ions come primarily from the ammonium carbonate.³ The ammonium carbonate concentration in the whetlerizing solution is about twice that of the chromate ion concentration, and this ammonium carbonate concentration permits the solubilization of $\text{Cu}(\text{NH}_3)_4^{+2}$. Gradual evaporation of the whetlerizing solution at room temperature results in the crystallization of compounds such as NH_4HCrO_4 , $\text{Cu}_4(\text{OH})_6\text{CrO}_4$, $\text{Cu}(\text{OH})_2\text{CO}_3$, and $\text{CuOHNH}_4\text{CrO}_4$.³ In contrast, the thermal treatment of the whetlerizing solution, during the preparation of the Type ASC whetlerite, results in amorphous materials. The infrared spectra of these amorphous materials indicate the presence of $\text{Cu}(\text{NH}_3)_4^{+2}$, $\text{Cu}(\text{NH}_3)_2^{+2}$, $\text{Cu}(\text{OH})^{+1}$, NH_4^+ , CrO_4^{-2} , HCrO_4^{-1} , and small amounts of CO_3^{-2} . The $\text{Cu}(\text{NH}_3)_4^{+2}$ appears to be preponderant.³

Type ASC whetlerite generally has a bifunctional activity. Its CK life seems to depend upon the basic and acidic sites on the whetlerite.⁶ Ammonium carbonate plays a role in the formation of the basic and acidic sites. Theoretically, the initial CK hydrolysis depends on the basic sites, whose chemical composition is $\text{Cu}_4(\text{OH})_6\text{CrO}_4\cdot\text{NH}_3\cdot\text{H}_2\text{O}$. Rapid hydrolysis of CK to OCN^- is further hydrolyzed by acidic sites such as NH_4HCrO_4 . Also, the CO_3^{-2} seems to play a role in the formation of the complex anion $(\text{CrO}_3 - \text{CO}_3)^{-2}$, which is believed to be a reactive acidic complex anion necessary for the whetlerite reactivity.⁶ Formation of this complex also imparts good stability towards aging.

As an amorphous material, activated carbon is highly negatively charged.³ Hence, the activated carbon is likely to adsorb positively charged rather than negatively charged complex ions. Complexing of copper ions with ammonia results in a rapid copper adsorption in the form of $\text{Cu}(\text{NH}_3)_4^{+2}$. Once the reactive, negative sites are saturated, an acidic site such as NH_4HCrO_4 is adsorbed by the charcoal. Thus, the complex formation of ammonium ions with chromium and copper permits deposition of these metal ions on the charcoal surface. In the presence of moisture, partial displacement of ammonia by water forms brochantite chromate, which is possibly responsible for rapid CK destruction.⁶ The carbonate ion permits the adsorption of chromium on the charcoal surface as well as renders the chromium reactive towards the cyanate anions by creating the catalytic species of the type $(\text{CrO}_3 - \text{CO}_3)^{-2}$.

The ammonium and carbonate ion's roles seem to be rather critical for the reactivity of agents such as CK. Attempts in the past to replace ammonium and carbonate ions have not been successful.⁷ For example, replacing NH_4^+ with ethylenediamine resulted in the loss of CK life. Similar attempts to replace Cu^{+2} in the complex $\text{Cu}(\text{NH}_3)_4\text{CrO}_4$ and CrO_4^{-2} with a stronger oxidizing anion also resulted in the loss of CK life.⁷ NH_4^+ seems to bridge the reactivities of Cu^{+2} and CrO_4^{-2} for hydrolyzing CK.

In summary, the freshly prepared Type ASC whetlerite contains the following copper-ammonium-chromium complexes:^{5,5}

- $\text{Cu}(\text{NH}_3)_2\text{CrO}_4$ -- most active
- $\text{Cu}(\text{NH}_3)_4\text{CrO}_4$
- $\text{Cu}_4(\text{OH})_5\text{CrO}_4 \cdot \text{NH}_3 \cdot \text{H}_2\text{O}$
- $\text{CuOHNH}_4\text{CrO}_4$
- NH_4HCrO_4 -- least active

2.4 Chemical Transformation on Whetlerite Involving Ammonia.

When exposed to conditions of relatively high humidity, ASC whetlerite gradually loses CK activity. Thus, water must be intimately associated with the chemical transformations of the reactive species present on the charcoal surface of ASC whetlerite. The metal-ammonia complexes mentioned earlier in this report have been implicated as primary targets for hydrolytic transformations. Complexes, such as $\text{Cu}(\text{NH}_3)_4\text{CrO}_4$ in contact with water, undergo a gradual ligand substitution that leads to the release of ammonia in the aqueous phase.³ The released ammonia can interact with water to form NH_4OH or escape due to its vapor pressure as ammonia gas. The basic copper-ammonium-chromate, $\text{CuOHNH}_4\text{CrO}_4$, could also undergo ligand exchange and lead to the release of ammonia. In both cases, the final product seems to be brochantite chromate $\text{Cu}(\text{OH})_6\text{CrO}_4$, which initially remains as amorphous and then gradually changes to crystalline material. Theoretically, the drop from pH 8 of freshly prepared whetlerite to pH 7.7 for whetlerite exposed to moisture is mainly because ammonia escapes.^{8,9} Thus, the hydrolytic transformation of the copper-ammonium-chromium complexes could release residual ammonia.

2.5 Studies on the Ammonium Desorption from Whetlerite.

As stated earlier in this report, although large amounts of ammonia in the form of ammonium hydroxide and ammonium carbonate are used for impregnating activated charcoal, very little ammonia is present in the freshly

prepared whetlerite. Although a detailed quantitative material balance for ammonia is not available at the present time, the ammonia gas is logically assumed not held by physical adsorption. The copper ammonium complexes can undergo chemical transformations as mentioned earlier, and these chemical transformations may lead to the conversion of the "chemically trapped" ammonia in the complex to aqueous ammonia, which may then be released or adsorbed as gaseous ammonia on the carbon surface.

Recently, some physico-chemical studies on desorption of ammonia have been carried out under different experimental conditions (conversation with R. Morrison, CRDEC). From the available data, temperature and humidity seem to affect desorption of ammonia from whetlerite. With increasing relative humidity (RH) at a constant temperature, there is an initial rapid release of ammonia from freshly prepared whetlerite, and this release decreases considerably over a period of several hours and levels off. At the same RH and as the temperature increases, the release of ammonia increases.

3. EXPERIMENTAL SECTION

3.1 Experimental Procedure.

Whetlerite samples were obtained from Calgon Corporation (Pittsburgh, PA) and exposed to either AC or CK until "breakthrough" occurred. The exposure procedures were the standard ones used at CRDEC.* The whetlerite samples were extracted with deionized distilled water (100 mL/g of whetlerite), and the pH of the solutions was determined (Table 1). The solutions were then treated with NaOH (1 mL, 10 m), and the released ammonia was measured using an Orion ammonia electrode (Orion Research, Incorporated, Cambridge, MA) (Table 2). All measurements were done in triplicate at room temperature (25 °C) with four different production lots tested.

Table 1. pH of Water Extracts from Whetlerite

Production Lot #	Mean \bar{x} , Standard deviation in parenthesis		
	Unexposed*	CK Exposed	AC Exposed
1	8.04 (0.02)	7.24 (0.04)	9.09 (0.04)
2	8.07 (0.02)	7.24 (0.02)	9.12 (0.03)
3	7.98 (0.04)	7.04 (0.01)	9.12 (0.07)
4	8.03 (0.02)	7.19 (0.02)	9.14 (0.04)

*All measurements were made in triplicate.

*For CK, 250 mL of charcoal is exposed to 50 L/min intermittent flow of air containing 4.0 mg/L of the toxicant. For AC, 12 g of charcoal is exposed in a tube to a constant flow of air (2.78 L/min) containing 10 mg/L of hydrogen cyanide.

Table 2. Ammonia Content in Water Extracts from Whetlerite (ppm)

Production Lot #	Mean %, Standard deviation in parenthesis		
	Unexposed	CK Exposed	AC Exposed
1	27 (1)	115 (1)	44 (2)
2	26 (1)	124 (1)	47 (3)
3	30 (4)	131 (3)	50 (2)
4	27 (3)	124 (5)	51 (4)

3.2 Results and Discussion.

The results show that during the exposure to AC and CK ammonia is being produced. The increased amount of ammonia results in more alkaline solutions of the AC exposed whetlerite (pH of about 9 versus pH 8) than in the unexposed whetlerite. The CK exposed whetlerite solution extract shows a significantly larger ammonia content, which is possibly attributed to the decomposition of cyanic acid reaction products that produces ammonia. The CK exposed whetlerite solution extract also has a pH of about 7 due to the production of HCL as proposed earlier.²

4. CONCLUSIONS

Activated charcoal impregnated with metal ions, such as copper and chromium, invariably uses ammoniacal solutions that permit a better pore deposition of the metal ions. Even after drying at elevated temperatures, a certain amount of ammonia is chemically trapped as copper ammonium chromate complexes. These complexes might be responsible, at least in part, for the residual ammonia desorptions and, therefore, pose possible problems associated with it. As discussed earlier in the report, ammonia is also released due to chemical reaction of the toxic gases on the charcoal surface. Presently, it is not clear whether ammonia is being produced from the AC or CK as a result of their reaction/decomposition on the surface, or if the reaction products of these gases causes trapped ammonia to be released. However, we believe that the former is more likely, because ammonia will not likely remain trapped on the charcoal after extraction with strong NaOH solution. Efforts to eliminate ammonia completely from the impregnating solution seem to be limited and have not been completely successful.¹⁰ Post-modification approaches to reduce the ammonia content by heating in the presence of moisture also seems to be less useful, as the whetlerite seems to lose its agent removal capability under such conditions. The main problem in reducing the ammonia content is the lack of detailed chemical information needed for our understanding of the active species role on whetlerite. A thorough understanding of these species might enable us to design methodologies to produce these active species without using ammonia either as a solubilizing agent or as a complexing ligand for generating the active species.

5. RECOMMENDATIONS

As discussed earlier, the metal ions are impregnated by deposition of an ammoniacal solution of these metal ions followed by thermal treatment. Several approaches can therefore be visualized to rectify the problem related to ammonia release from whetlerite. The first approach would be to optimize the amount of ammonia required for the initial solubilization of the metal ions. A careful study of the literature indicates that this has indeed been done with respect to Cu-ammonia-Cr ratio.² However, the total ammonia content of the whetlerite samples seems to be very little. Therefore, during this processing, all the excess ammonia is eliminated. Ammonia is present on the whetlerite samples mainly as copper chromium complexes. Because these

complexes are implicated in the catalytic efficiency of the whetlerite, any treatment such as thermal would result in the loss of CK activity. Therefore, further improvement of the impregnation process is unlikely to provide solutions to the problems related to the ammonia release.

Another promising approach would be to perform post-modification of Type ASC whetlerites to reduce the ammonia release either totally or to an acceptable level. Heat and water affect the ammonia release from Type ASC whetlerite. Heating whetlerite samples releases ammonia; such pretreatment prior to the samples' use in gas masks may reduce the level of ammonia released. Likewise, a pretreatment with water could, in principle, be used to reduce the ammonia desorption levels. The major disadvantage of such a modification is that the whetlerite will lose CK activity concomitantly. In other words, the crux of the problem is that heat and water pretreatment would be detrimental to the CK life of whetlerites. The solution to the problem requires an approach that would remove residual ammonia without promoting the loss of catalytic sites on the surface of impregnated charcoal. The relationship between the loss of CK activity and decrease in ammonia content, due either to aging or to pretreatment with water and heat, is not very clear. Ammonia may then be playing a role in maintaining the copper chromate species that are alleged to be necessary for the catalytic activity.⁵ Another view is that ammonia maintains a basicity on the whetlerite surface that in turn prevents deterioration.⁴

Another approach to this problem is to investigate whether copper chromium complexes, containing other ligand but similar to the above mentioned ammonia complexes, would result in catalytically active species. In such studies, the overall mechanism of ammonia release should be considered. It is believed that in the case of metal-ammonia complexes, ligand exchange leads to the release of ammonia into the aqueous phase, which then equilibrates partly as gaseous ammonia that may be held adsorbed on the whetlerite surface. Use of ligands that may undergo a similar process, but do not desorb due to their high boiling points and molecular weights, should be carefully investigated.

All the approaches to rectify release from whetlerite have a major weakness of being empirical in nature. The approaches all lack or take little consideration of the chemical nature of the catalytically active species or sites and the role of ammonia and the mechanism of its release. We firmly believe that approaches either to eliminate ammonia totally from the impregnating solution or to reduce it by post-modifications should be based on these mechanistic and chemical insights.

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